THE FATE OF SCALE INHIBITORS IN OIL/GAS PRODUCTION

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ABSTRACT

The thermodynamic properties of the scale inhibitor, phosphino-polycarboxylic acid (PPCA) and of its calcium complexes under conditions of high ionic strength and high temperature have been studied by potentiometric titration. Applying the electrostatic theory for polymers gives dissociation constant K_M for $ML \leftrightarrow M+L$ as $pK_M=pK_{Mint}+zf\theta_u$ where L stands for polymer ions, pK_{Mint} stands for intrinsic constant, z is the charge of the small ion M which can be H^+ and any metal ion, f is a parameter related with polymer characteristics and θ_u stands for the dissociation fraction of the polymer ion. A general equation for f is obtained: $f=2.757-1.056I^{1/2}+0.220I$ where I stands for ionic strength. The intrinsic constant for proton dissociation pK_{Hint} (when M is proton) is assumed to be: $pK_{Hint}=4.798-0.954I^{1/2}+0.246I-187.8/T$ where T stands for temperature in Kelvin. For calcium ion (M is Ca^{2+}), the intrinsic constant is: $pK_{Mint}=3.928-2.631I^{1/2}+0.738I-1099.4/T$. Also investigated are calcium-PPCA precipitation and dissolution. An empirical dissolution reaction is observed as: $Ca_3(A\text{-}A\text{-}A)_{2\,(S)} \leftrightarrow 3Ca^{2+}+2(A\text{-}A\text{-}A)$, of which the solubility product $Ksp=[Ca]^3[A\text{-}A\text{-}A]^2$ can be expressed as: $pKsp=34.02-0.832I^{1/2}+0.762I-6839.5/T$. Here, (A-A-A) stands for an arbitrary unit of three functional groups (A). Therefore, PPCA concentration and its species distribution in any oil/gas production can be predicted by these equations and consequently the efficiency of PPCA as a scale inhibitor for a specific well can be evaluated and can be applied in squeeze design.

INTRODUCTION

Phosphino-polycarboxylic acid (PPCA), $H\text{-}\{CH_2CHCOOH\}_x\text{-}POOH\text{-}\{CH_2CHCOOH\}_y\text{-}H$, is different by only one group (phosphino group) from polyacrylic acid (PAA). It is widely used in oil fields as a scale inhibitor because of its good quality, low cost and environmental acceptability. Chang and Patel (1) have studied PPCA under typical boiler conditions and found that as a scale inhibitor (for $CaCO_3$, calcium hydroxyapatite and iron oxide), PPCA has advantages over PAA and phosphonates in thermal stability, dispersion and iron transport. Some other research (2,3) implies that PPCA or its derivatives have potential to be multifunctional inhibitors in boilers, cooling water formulations and oil wells. Rabaioli and Lockhart (4) have investigated the precipitation conditions and precipitate yield of CaPPCA and its solubility in a brine system. The sharp contrast of high solubility to the observed very low concentration of inhibitors in the return produced water of oil wells was explained as a kinetically controlled dissolution.

Taking into consideration the great potential of application of PPCA in many aspects and the variety of the conditions of those applications, this paper tries to explore the fundamental aspects of the solution chemistry of PPCA under various harsh conditions and to provide basic data for its application. This includes constants of proton dissociation, metal complexation of PPCA, and precipitation/dissolution of CaPPCA. They all together determine the efficiency of PPCA as a scale inhibitor and the lifetime of a squeeze.

In structure, PPCA is similar to PAA which is used as a standard polymer for studying properties of linear polyelectrolytes. For this reason, the basic concept in this study is transplanted from those developed for PAA. On the base of research by Debye and Huckel (5), Falkenhagen (6), Kirkwood and Poirier (7), Hill (8), Hermans and Overbeek (9), Tanford (10,11) et al, applying electrostatic theory to PPCA, one can easily derive the following hypothetical reaction and their constant expressions:

$$ML \leftrightarrow L + M, \quad pK_M \qquad (1)$$

$$pK_M = -\log\frac{[M][L]}{[ML]} = pM - \log\frac{\theta_u}{\theta_M}$$

$$= pK_{M\,int} + zf(R,r,\kappa)\theta_u \qquad (2)$$

where L is an arbitrary combined unit of z functional groups (monoacids, A), L=zA and [L]=[A]/z, and ML is electroneutral. M with charge z represents any cation which can associate with PPCA. For instance, when M stands for proton, H^+, z=1 and L is just one group while for Ca^{2+}, z=2 and L is an arbitrary unit of any two groups. The parameter f is a function of the polymer size R, small cation (M) size r and Debye-Huckel parameter κ which is then related with ionic strength. Of course f is also a function of temperature. pK_{Mint} is the so-called intrinsic constant. θ_u stands for dissociation fraction of PPCA, $\theta_u=z[L]/C_A=[A]/C_A$ while θ_M stands for

the association fraction of PPCA by M, $\theta_M = z[ML]/C_A$ with C_A meaning total PPCA concentration in normality.

The second term in equation 2 represents the electrostatic effect of neighboring dissociated groups on the given group. Under certain conditions, R might be independent of the dissociation fraction so that $zf(R, r, \kappa)$ in the second term of equation 2 might be a constant through a titration. Therefore, pK_M is linear to dissociation fraction θ_u. Applying this to titration data can yield pK_{Mint} and $f(R, r, \kappa)$ from a plot of pK_M versus θ_u.

After pK_Ms are available, precipitation/dissolution of metal polymer precipitates can be analyzed. However, this equilibrium is very complicated and no definition of solubility product for metal polymer precipitates is available from literature. Therefore, a hypothetical precipitate and its dissolution equilibrium are assumed to be:

$$M_mL_{l\,(c)} \leftrightarrow mM + lL\,,\ K_{sp} \qquad (3)$$

$$K_{sp} = [M]^m[L]^l \qquad (4)$$

where L is an arbitrary unit (statistically) of x As (univalent). Therefore, L=xA and [L]=[A]/x. Furthermore, the electroneutrality requires xl=mz. Thus equation (4) becomes:

$$K_{sp} = [M]^m\,[A]^l\,(\frac{1}{mz})^l \qquad (5)$$

or

$$\log[A] = \{\frac{\log(K_{sp})}{l} - \log(\frac{1}{mz})\} - \frac{m}{l}\log[M]$$

$$= \text{constant} - \frac{m}{l}\log[M] \qquad (6)$$

Equation (6) shows that m and l can be obtained from the plot of log[A] vs. log[M]. In this plot, the slope is -m/l. Since m, l and x should be integral, m/l is the common fraction of the slope. For example, if the slope is -m/l=-0.33, take l=3, m=1, and x=0.333z, thus z must be 3; if -m/l=-1.5, then take l=2, m=3, and x=1.5z.

EXPERIMENTAL

Chemicals: Phosphino-polycarboxylic acid (PPCA) was from FMC Co., 50%, MW ~3600. NaCl, used for adjusting ionic strength, was from Fisher Scientific Co., 99.4%. $CaCl_2{\cdot}2H_2O$, used for titration , precipitation and stock solution, was from Fisher Scientific Co., 76.1% ($CaCl_2$). Acid/base titrant of 1.600±0.008 N and 0.1600±0.0007 N NaOH cartridges and EDTA titrant cartridges were from HACH Co. All stock solutions were made with deionized water.

Potentiometric titration: Solutions of different concentration of PPCA with or without Ca^{2+} were titrated by NaOH in a jacketed beaker. The ionic strength of the solutions was adjusted by NaCl and the temperature was monitored by a temperature circulator within ±0.1 °C. Each titration was finished under a fixed condition. pH was measured by an Accumet model 15 pH meter (Fisher Scientific Co.) with a Ross combination pH electrode (Orion Inc.). Before each titration, the pH electrode was refilled with new filling solution (Orion Inc.) and was kept in a storage solution at the same temperature for about 2 hours to be stabilized. Immediately before and after each titration, the stabilized pH electrode was calibrated. All operations relevant to titrations were run under N_2 atmosphere.

Precipitation/solubility product: Precipitation was carried out by slowly titrating PPCA solution [using a syringe pump (Harvard Co.)] into a bulk solution of 1N NaCl-$CaCl_2$-1mM NaAc at pH5.5 and 70°C under stirring. The Ca^{2+} concentration was made so that after equivalent precipitation, the remaining Ca^{2+} concentration in solution was 0.1M. pH was simultaneously monitored at pH 5.5. After the titration precipitation was finished, the slurry was kept stirring about 5 hours and then transferred into an Amicon cell fitted with an Amicon YM 10 membrane to do diafiltration/maturation under 70°C and stirring for a week with an inflow of stock solution of 1N NaCl-0.1M $CaCl_2$-1mM NaAc at pH5.5 and 70°C. The flow was monitored by a pump (Pharmacia LKB) at about 90 ml/hr. After a week, the produced solids-solution mixture was kept in a 70°C oven for static maturation. Samples were taken at different stages to study the evolution of the stoichiometry of the precipitate and its solubility. All solid samples were put through a 0.2 μm microfilter and washed with deionized water many times at the same temperature. Solids collected in this manner were used to study the stoichiometry while the filtrates were collected for quantitative analyses to provide data for the study of thermodynamic properties. Also the samples at different stages were used to explore the relationship between the solubility and other condition variables, such as ionic strength, temperature and different Ca^{2+} concentrations.

RESULTS AND DISCUSSION

The plots of acid/base titration curves (pH vs. dissociation fraction, θ_u) at different ionic strength and temperature in the absence of Ca^{2+} are shown in figures 1 and 2, respectively. As the figures show, with an increase of ionic strength, pH decreases (figure 1)with the same dissociation fraction, implying that the dissociation constant decreases. While temperature has little effect on the PPCA association/dissociation (figure 2). Data treatment shows that pK_H is linear with θ_u in the range of dissociation fraction 0.3 to 0.95, especially at higher ionic strength ([NaCl]>0.05M). This observation is consistent with that by Miyajima et al (12) for PAA and other observations (13,14,15,16). It was also observed that the concentration of polyacid has a slight influence on the dissociation constant but at a higher concentration and higher ionic strength, pK_H has no significant change with concentration, which is consistent with findings for PAA by Nagasawa et al (12), Arnold and Overbeek (17), and Samelson (18). Quantifying all relationships between the dissociation constant and condition variables by the nonlinear regression method, a general equation for proton dissociation of PPCA acid was obtained:

$$pK_H = (4.798 - 0.954\sqrt{I} + 0.245I - \frac{187.8}{T}) + (2.757 - 1.056\sqrt{I} + 0.220I) * \theta_u \qquad (7)$$

From this equation, it is easy to get $pK_{Hint}(I=0,T=298K)=4.17$ for PPCA which is smaller than $pK_{Hint}=4.28$ for PAA by other researchers (13), $pK_H=4.76$ for acetic acid and $pK_{Hint}=4.64$ for glutaric acid under the same conditions.

Figures 3 and 4 show the similar titration curves but at the presence of Ca^{2+}. Applying equation 2 and equation 7 to these titration curves, a general equation was then obtained by least square method:

$$pK_M = (3.928 - 2.631\sqrt{I} + 0.738I - \frac{1099.4}{T}) + 2(2.757 - 1.056\sqrt{I} + 0.220I) * \theta_u \qquad (8)$$

This equation gives $pK_{Mint}(I=0, 298K)=0.24$, comparing with $pK_M=1.06$ for glutaric acid (H_2L)-calcium complexation (19) and 1.16 for succinic acid-calcium (20). But extrapolation to I=0 for both pK_{Hint} and pK_{Mint} should be careful since no titration is carried out at very low ionic strength where constants are extremely sensitive to that.

Once both pK_H and pK_M are set up, solution equilibria analysis can be done for a Ca-PPCA solution system. Sampling the long-time matured precipitates, solubility experiments under wide diverse conditions were carried out. The solid speciation indicated that these long-matured precipitates are composed of only Ca and PPCA and the ratio is: Ca:PPCA=1:1 (in equivalence). The formula can thus be written as: $[Ca(CH_2CHCOO)_2 \cdot xH_2O]_n$ (-POO-). Figure 5 shows the results of the dissolution experiments on these precipitates designed for solubility product at pH 5.5, 70°C and in 1.0m NaCl solution. It implies that the product $[Ca]^{1.5}[A]$ or $[Ca]^3[L]^2$ is constant (A represents free monomer, L represents a unit of certain monomers). Considering electroneutrality and applying equations (5) and (6), we let l=2, m=3, and x=3 and the precipitate of CaPPCA behaves like the simple crystals of calcium-trimer precipitate. Applying this semi-empirical definition of solubility product to solubility data, a plot of pK_{sp} vs. ionic strength at differing temperature was obtained as in figure 6. And further nonlinear regression analyses yield the equation:

$$pK_{sp} = 34.02 - 0.832\sqrt{I} + 0.762I - \frac{6839.5}{T} \qquad (9)$$

It should be pointed out that at a different temperature, the crystalline morphology of the precipitates might be different. This equation might therefore not reflect the real physical details of pK_{sp} but just a mathematical expression. However, the equilibria calculations showed that the calculated solubility of CaPPCA is very close to the experimental result, and more than that, is reasonably consistent with that of CaPAA from literature (21).

The predicted titration curves by these numerical equations also show the very good consistency with titration data, as shown by lines in figures 1 and 3.

With these constants, one can evaluate the feasibility of PPCA as a scale inhibitor in a specific well. Table 1 gives 3 field case studies. In this table, 'equil PPCA' means the equilibrium concentration of PPCA calculated from those equations above under the well condition and 'min PPCA' means the minimum PPCA concentration required for inhibiting scale formation in this specific well and is calculated from the Scalesoft™ (A scale control and treatment software produced by the Brine Chemistry Consortium in Rice University). In well #1,

PPCA can not be applied as an inhibitor in a precipitation squeeze because the equilibrium concentration can not meet the minimun concentration needed. Well #2 doesn't need any inhibitor. PPCA can work well as a scale inhibitor in Well #3. However, further reasearch need to be done at extremely high temperature where the polymer properties might change and extended application of these equations might be inappropriate.

Table 1. The equilibrium concentration (available) and the minimum concentration (required) of PPCA as a scale inhibitor in three oil wells' production assuming precipitation squeeze.

Well	Ca (M)	I (M)	T (K)	pH	equil PPCA, (ppm)	min PPCA, (ppm)
#1	0.240	2.91	424.7	5.5	0.0012	11.15
#2	0.0307	1.20	411.9	6.0	0.10	0
#3	0.0112	0.74	371.9	6.5	3.92	3.51

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REFERENCE

[1]. Kelvin Y. Chang and Suresh Patel. A Mechanistic Study of Phosphinocarboxylic Acid for Boiler Deposit Control. MP/July 1996, p.48-53.

[2]. T. Grchev, M. Cvetkovska and J. W. Schultze. The Electrochemical Testing of Polyacrylic Acid and Its Derivatives as inhibitors of Corrosion. Corrosion Science, Vol 32, No 1, 103-112, 1991.

[3]. S. Patel and A.J. Nicol. Developing a Cooling Water Inhibitor with Multifunctional Deposit Control Properties. MP/June 1996, p.41-47.

[4]. M.R. Rabaioli, Thomas P. Lockhart. Solubility and phase Behavior of Polyacrylate scale inhibitors. J. petroleum Sci and Engin 15(1996) 115-126.

[5]. P. Debye and E. Huckel, Physik. Z., 24, 185 (1923).

[6]. H.S.Harned and B.B. Owen, Physical Chemistry of Electrolytes, 2nd ed., Reinhold Publishing Corp., New York, 1950, Chs2,3.

[7]. J.G. Kirkwood and J.C. Poirie, J. Phys. Chem., 58, 591 (1954).

[8]. T.L. Hill, Arch. Biochem. Biophys., 57, 229 (1955).

[9]. J.J. Hermans and J. Th. G. Overbeek, Rec. trav. chim., 67, 761 (1948).

[10]. C. Tanford, J. Phys. Chem., 57, 229 (1955).

[11]. Charles Tanford, Physical Chemistry of Macromolecules, Joh Wiley & Sons, Inc., 1967.

[12]. Tohru Miyajima, Megumi Mori and Shin-ichi Ishiguro, Journal of Colloid and Interface Science, 187, 259-266 (1997).

[13]. R. Arnold and J.Th.G. Overbeek, Rec. trav. chim., 69,192(1950)

[14]. D.T.F. Pals and J.J.Hermans, Rec. trav. chim., 71, 433 (1952)

[15]. V.Ya. Kabo, L.A. Itskovich and V.P.Budtov, Polym Sci USSR 31,10, 2217(1989)

[16]. K.R.Rogan, Colloid Plym Sci 273: 364-369 (1995)

[17]. R. Arnold and J.Th.G. Overbeek, Rec. trav. chim., 69,192(1950)

[18]. Samelson,H., Columbia Univ. thesis; Univ. Microfilms (Ann Arbor, Michigan), Publ. No. 9531 (1954).

[19]. R.K. Cannan and A. Kibrick, J. Amer. Chem. Soc., 1938, 60, 2314.

[20]. H. morawetz, A.M. Kotliar and H. Mark, J. Phys. Chem., 58, 619 (1954).

[21]. Tsuneo Okubo and Nobuyuki Mohri, The Solubility of Polyelectrolyte Complexes. CalciumPolyacrylate and the Poly(4-Vinyl-N-pentylpiridinium) Salt of Poly(styrenesulfonic Acid). Macromolecules 1988, 21, 2744-2747.

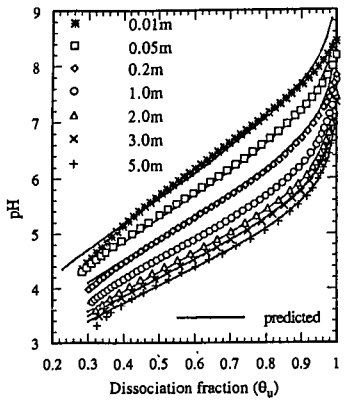

Figure 1. Plot of pH vs θ_u for acid-base titration of 0.0025N PPCA at 70°C and different NaCl concentration

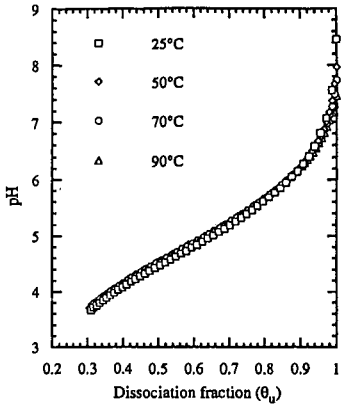

Figure 2. pH vs θ_u for acid-base titration of PPCA solution: 0.0025N PPCA-1.0m NaCl at different temperatures.

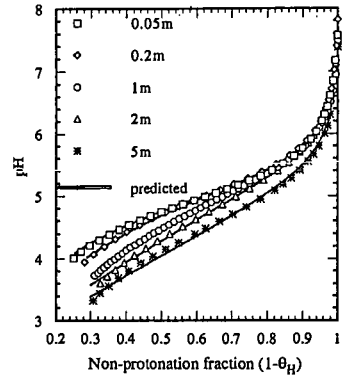

Figure 3. Plot of pH vs ($1-\theta_H$) for the acid-base titration of 0.0025N PPCA-0.005M Ca solution at 70°C and different NaCl concentration.

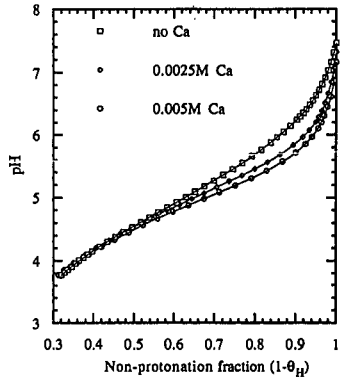

Figure 4. pH vs ($1-\theta_H$) for acid-base titration of 0.0025 N PPCA solution at 90°C and 1m NaCl.

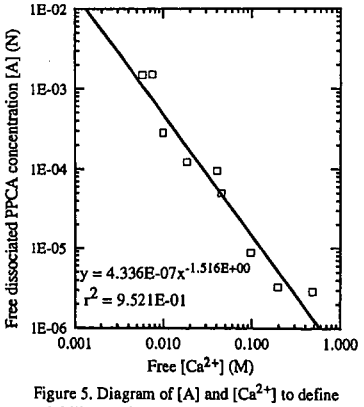

Figure 5. Diagram of [A] and [Ca^{2+}] to define solubility product of Ca-PPCA.

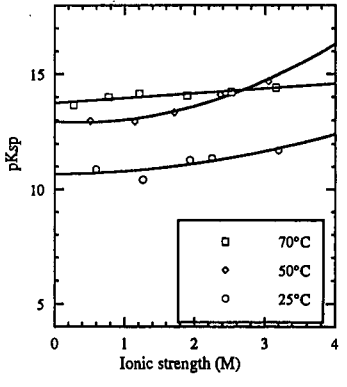

Figure 6. Diagram of pKsp of Ca-PPCA vs. ionic strength at three different temperatures.